Review

Catalytic synthesis of polyoxymethylene dimethyl ethers (OME): A review

Christophe J. Baranowski[a], Ali M. Bahmanpour[a], Oliver Kröcher[a,b,*]

[a] *Institute of Chemical Sciences and Engineering, Eícole polytechnique feídeírale de Lausanne (EPFL), 1015 Lausanne, Switzerland*
[b] *Paul Scherrer Institut, OVGA/112, 5232 Villigen PSI, Switzerland*

ABSTRACT

Polyoxymethylene dimethyl ethers (OME) containing 3–5 CH_2O units (OME_{3-5}) are appealing oxygenated fuels, which can be used in diesel engines with only slight fuel system modifications. Their combustion leads to reduced hazardous exhaust gas emissions compared to standard diesel. Due to the absence of C-to-C bonds, they considerably reduce soot formation, allowing in turn significantly higher exhaust gas recirculation (EGR) rates to reduce NO_x emissions. Established liquid-phase OME production processes involve trioxane as a costly intermediate. Moreover, the OME product equilibrium composition follows a Schulz-Flory distribution making selective synthesis of specific chain length cumbersome. Current research efforts focus on simplifying the existing processes by using fewer steps, simpler reactants and less energy. Several catalyst classes were reported to catalyze OME acid synthesis. Little is known about the reaction mechanisms and the elementary steps involved. This review highlights the need for more systematic research on new reactants, efficient catalysts and simpler processes.

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1. Introduction

Diesel engines have a higher thermal efficiency than gasoline engines due to their higher pressure and temperature. However, the combustion of diesel fuel lead to hazardous exhaust gas emissions, which contribute to air pollution [1]. These exhaust emissions are classified as carcinogenic to humans by the International Agency for Research on Cancer [2]. In this context, polyoxymethylene dimethyl ethers (OME, also referred to as OMEs, POME or POMDME in the references) have recently received increasing attention, since various studies [3–10] demonstrated that a blend of OME with diesel fuel reduces soot particles formation, unburned hydrocarbons and carbon monoxide emissions during combustion. At the same time, nitrogen oxide emissions (NO_x) remained at a similar level, at which both slight increase [4,9,10] and decrease [8,11] have been reported.

OME, shown in Fig. 1, are oligomers composed of CH_2O units, which are highly stable since their chains are capped with one methyl and one methoxy group. The oxymethylene chain of variable length dictates the molecule properties.

A particularly attractive property of OME is that the blends of diesel fuel and OME with the appropriate chain length can be used in slightly modified diesel engines [4]. Their properties, notably boiling point, cetane number and viscosity, can be controlled via the chain length. Their large scale usage therefore requires no modifications to the fuel distribution infrastructure and only slight adjustment to the injection system. If produced from renewable sources such as biomass, their usage may reduce the global CO_2 emissions compared to fossil fuels in addition to their emission reduction effect [12].

Biofuel usage will become mandatory in many areas of the world such as in the European Union with a ratio of 10% of biofuels for transport by 2020 [13]. The current source of biodiesel is mainly first generation biofuels such as fatty acid methyl esters (FAME) biodiesel. However, their usage was shown to increase CO_2 emissions up to 20% compared to oil-based diesel when effects of indirect land use are considered [14]. OME may provide a sustainable alternative to first generation biofuels and part of the fossil fuels.

OME are synthesized from methanol, which can be produced via biomass gasification and subsequent syngas conversion. Methanol is a versatile chemical considered for storing renewable energy and a product of CO_2 recycling processes which constitutes the basis of the methanol economy [15]. The different ways methanol is produced and used in the OME synthesis processes are shown in Fig. 2. Several combinations of reactants are available to synthesize OME. Formaldehyde is produced through methanol oxy-dehydrogenation process, which is then used to produce trioxane (TRI) or paraformaldehyde (PF). Dimethoxymethane (OME_1, also referred to as DMM in the references) is the shortest OME and is synthesized from methanol and formaldehyde by reactive distillation. Current trends highlight the shift of focus towards production processes requiring less steps and simpler reactants such as dimethyl ether (DME), methanol or aqueous formaldehyde.

Researchers have proposed various OME production methods using ion exchange resins as well as ionic liquids as catalysts [16,17]. Considering the undesirable formation of byproducts,
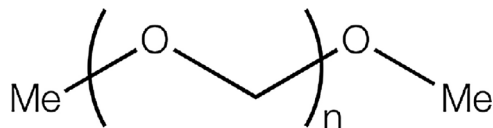
energy intensive separation steps are required to obtain concentrated, high-quality OME of the desired chain length. The first efforts to synthesize OME were accomplished as early as 1904, when Descudé prepared OME_2 by reaction of dichlorodimethyl ether and sodium methylate [18]. In the 1920s, Staudinger and Luthy [19] systematically investigated their properties and synthesis. High molecular weight polyoxymethylene ethers are interesting polymer materials, called POM, and in the middle of the 20th century several companies, notably DuPont in the 1960s, invented production processes to obtain thermally stable POM polymers [20]. Boyd determined some physico-chemical properties of OME_{2-5} [21]. As oxygen-containing compounds demonstrated promising combustion and emission properties, interest in OME production started at the beginning of the 21th century. BP corporation [22–29] patented various production methods from several reactant combinations from 1999 to 2003, followed from 2007 to 2011 by BASF [30–33] and others [34,35]. Recently, Chinese academics and industry have been very active in methanol and dimethyl ether synthesis from coal [36]. They have therefore taken the lead, in terms of number of publications or patents, on the development of OME as a solution to use their coal feedstock and alleviate their air pollution problems. Shandong Yuhuang Chemical Co. inaugurated an OME synthesis plant in 2015 based on a fluidized-bed reactor process [37,38]. To the best of our knowledge, it is the only reported OME production facility alongside with pilot plants projects in Germany [4,9,10,39–42]. Recently, interest in Germany in OME production has regained much interest, reflected in these pilot activities and a rapidly increasing number of publications, however, with a focus on carbon-neutral production of OME in contrast to the Chinese focus on coal as primary carbon source.

Even though OME synthesis is relatively easy and involves catalytic steps, the current production routes are either expensive or energetically rather inefficient, leading to uneconomical production or modest CO_2 footprints, respectively. A recent study from Schmitz et al. assessed the production costs of large-scale OME production [43]. The major costs were predicted to be of around 60% for raw material and 20% for energy consumption. Large-scale production of OME requires technically feasible processes and economically viable prospects. Furthermore, more suitable catalysts have to be developed for these processes and more research on the reaction mechanism is necessary. Although much literature is now available on liquid-phase and batch reactor synthesis, research is still required on the scale-up to larger, continuous processes. This paper reviews the literature on OME synthesis with the objective to stimulate new insights into and new ideas for catalytic processes to this fascinating type of fuel molecules. We will begin by briefly discussing the properties of OME as fuel additives. The main synthesis routes will then be delineated and the catalysts used and their performances will be described. Finally, a short discussion of the proposed mechanisms will be provided.

2. OME properties as synthetic fuel

There have been many investigations on the usage of oxygen-containing compounds (oxygenates) as fuels or additives to conventional fuels in spark-ignition engines. They were initially of interest for their high octane numbers as anti-knocking agent to replace tetraethyl lead with oxygenates such as methyl tertiary butyl ethers [44]. Further research on fuels containing a higher weight percentage of oxygen demonstrated their soot reduction properties during combustion in diesel engines [45].

The simplest oxygenates with a higher oxygen weight percentage are dimethyl ether and methanol. The former has a high cetane number, a low autoignition temperature and combusts almost
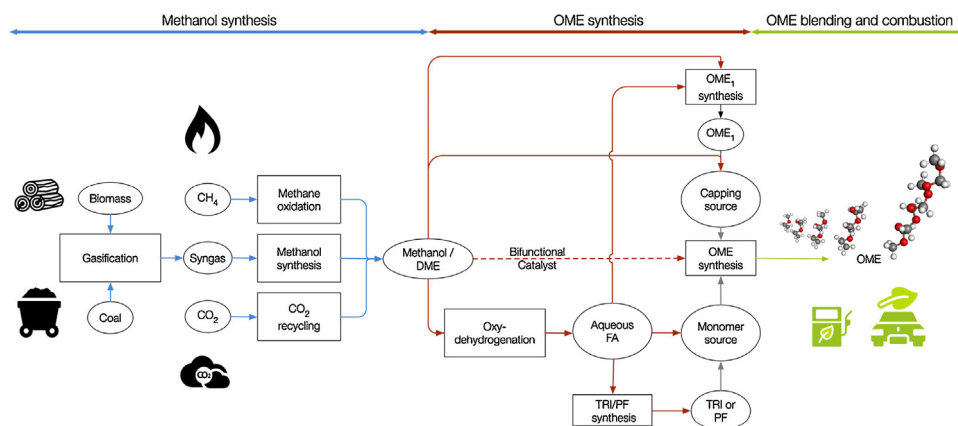
Fig. 1. Structure of polyoxymethylene dimethyl ethers (OME). $OME_n = H_3C(-O-CH_2)_n-CH_3$.

Fig. 2. Liquid phase synthesis routes to polyoxymethylene dimethyl ethers (OME) via methanol derived from various sources. The depicted routes and reactants have been reported to be used for the production of OME_n with $n > 1$: OME_1 = dimethoxymethane, TRI = trioxane, PF = paraformaldehyde, FA = formaldehyde, DME = dimethyl ether.

soot-free in compression-ignition engines [46]. The latter, despite its lower energy density has an inherent higher efficiency thanks to its high cetane number [44]. However, they both have drawbacks that requires adaptation of fuel tanks or engines to store or use them [46]: methanol is toxic, exhibits incompatibility to certain materials and encounter cold-start problems; DME is gaseous at ambient temperature and has a miscibility gap with diesel fuel at temperature under $0\,°C$. Their large-scale usage thus requires considerable modification to engines or fuel distribution infrastructures. In comparison, OME are liquid, non-toxic and demonstrate good material compatibility. Additionally, there is no miscibility gap between OME and diesel fuel [47]. Due to these advantageous properties, engine performance tests, combustion and emission characteristics of various mixtures of fuels and OME have been reported in literature.

2.1. Physico-chemical properties

A fuel must comply with regulation and specifications depending on countries such as EN 590 for European countries. Several studies showed that OME_{3-5} are suitable fuel additives complying with such regulations [7,9,10,47,48]. OME have chemical properties, summarized in Table 1, closer to paraffinic diesel fuel and may thus comply to EN15940 standard [49]. OME_{3-5} display cetane numbers of 67, 76 and 90 [7], which are all higher than the minimum required by the EN 590 for commercial diesel [50]. Their flash points range from 53.5 to $115.0\,°C$ [7], mostly meeting the lower limit of $55\,°C$ enforced by the EN 590. Long-chain OME with $n > 5$ precipitate at temperatures below $18\,°C$ leading to a risk of blocking the fuel filter if used [7]. On the other side, short-chain OME with $n < 3$ have a lower viscosity than diesel fuel that may require injector modifications. They also have a lower vapor pressure and flash point than diesel hence not fulfilling this safety criterion [4,47]. However, all their other physico-chemical properties, e.g. viscosity, lubricity, are mostly similar to standard diesel fuel allowing its usage without modifying the diesel engines. Additionally, if produced from natural gas, their low sulfur content meets even most stringent fuel requirements for sulfur content [4,51]. Finally, OME may contain residual trioxane and formaldehyde. The maximum allowed concentration of these toxic residues will need to be standardized [49]. OME_{3-5} are thus suitable fuel additives to use in diesel engines with only slight modifications of the fuel supply system.

Lautenschütz et al. also studied the physico-chemical properties of polyoxymethylene diethyl ethers (OMEE) [7]. The most distinctive characteristic is their autoignition point. OMEE exhibit lower autoignition points due to the possible peroxy radical forma-

tion that can trigger decomposing chain reactions in the presence of oxygen. $OMEE_{2-4}$ exhibit a flash point range of $35.3–94.5\,°C$, approximatively $20\,°C$ lower than that of OME_{3-5}.

2.2. Combustion and emission characteristics

CO_2-neutral, infinite supply, minimum well to wheel emissions, cost-effectiveness, and functionality are the five conditions of the future sustainable energy and fuel systems [53]. OME are shown to be compatible with the conditions in various studies [52,54]. OME have a lower heating value and energy content compared to conventional diesel fuel due to their oxygen content. Their usage thus increase volumetric fuel consumption [4]. Increasing the OME ratio in diesel fuel blends shortens the main combustion delay due to the increase of the mixture's cetane number. At loads higher than 6 bar IMEP, a longer main combustion delay has been reported [9]. When a diesel engine runs at high load, large amount of fuel is injected into the combustion chamber resulting in fuel-rich regions favorable for pyrolysis which results in soot particles formation. OME do not contain carbon-to-carbon bonds, which are the most basic structural elements of soot, hence reducing the amount of soot particles emission [6]. Besides, soot precursors are degraded by hydroxyl radicals formed during combustion of OME [55]. The reduced soot-forming potential allows higher exhaust gas recirculation (EGR) rates which also reduces the NO_x emissions. The NO_x/particulate trade-off is thus mitigated by the addition of OME to the conventional diesel fuel as shown in Fig. 3.

Various studies confirmed the OME influence on combustion emissions. Ianuzzi et al. observed a nearly soot-free combustion for pure OME combustion in a constant volume chamber [6]. They also demonstrated that the addition of 5% of OME_2 to commercial diesel fuel leads to 30% reduction in soot emissions. Based on their research, the correlation between fuel blend oxygen content from the addition of OME and the decrease in soot particle emission is non-linear. Lumpp et al. compared combustions and emissions of diesel fuel with a blend of 20 vol% of OME_{3-4} to pure diesel fuel using a six-cylinders engine [5]. Compared to diesel fuel emissions, soot particle emissions from the combustion of the fuel blend decreased by 60% and 50%, respectively, during European stationary cycle and light European transient cycle tests. The gravimetric particulate mass decreased by 40% and 25%, respectively. In addition, the particle number respectively decreased by 50% and 40%. They also compared the emissions of a blend of 10 vol% OME_2 and diesel fuel with the emissions of the pure diesel fuel on a single-cylinder using various engine speeds and loads. They observed a decrease of soot emissions between 30–40% with an adjusted EGR to have similar NO_x emissions.

Table 1
OME Properties (from ref. [52]).

|	OME$_1$	OME$_2$	OME$_3$	OME$_4$	OME$_5$	OME$_6$
CAS No.	109-87-5	628-90-0	13353-03-2	13352-75-5	13352-76-6	13352-77-7
Molecular Formula	$C_3H_8O_2$	$C_4H_{10}O_3$	$C_5H_{12}O_4$	$C_6H_{14}O_5$	$C_7H_{16}O_6$	$C_8H_{18}O_7$
Oxygen Content (%)	42.1	45.2	47	48.1	48.9	49.5
Boiling Point (°C)	42	105	156	202	242	273
Melting Point (°C)	−105	−70	−43	−10	18	38
Cetane Number	29	63	67	76	90	NA
Lower Heating Value (MJ/kg)	22.4	20.6	19.4	18.7	18.1	17.7
Density (kg/m^3)	860	980	1030	1070	1110	1140
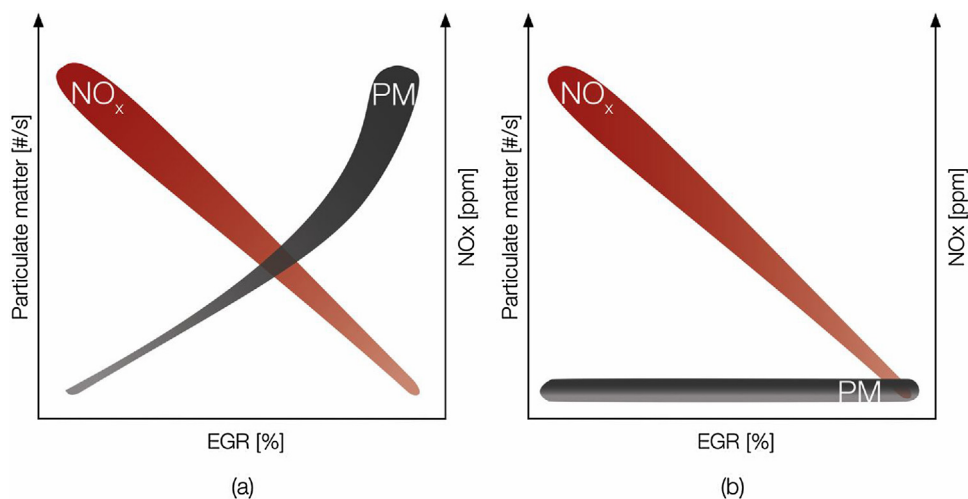
Fig. 3. Schematic representation of particulate matter (PM) and NO$_x$ versus exhaust gas recirculation (EGR) in a compression ignition engine for the combustion of (a) diesel and (b) pure OME.

In subsequent studies, Liu et al. investigated the engine performance and emissions characteristics of blends of OME$_{3–4}$ with diesel fuel and gasoline-diesel in a single-cylinder engine [4,9,10]. They stated that the addition of OME$_{3–4}$ reduced soot particles formation to a large extent. They claimed a soot-free combustion by using a 20 vol% OME$_{3–4}$/diesel blend. Conversely, other studies showed that pure OME are required to remove soot formation completely [8,52,56]. NO$_x$ emissions increased slightly with increasing OME ratio; they therefore identified the 20% blend value as optimal as it minimizes NO$_x$ and soot particles emissions. Simultaneously, CO emissions decreased drastically by 90% at high loads (mean effective pressure of 8 bar), but hydrocarbon emissions were only slightly reduced. Tests of a blend of OME$_{3–4}$/diesel/gasoline with a 30/35/35 vol ratio showed similar emission trends. However, addition of gasoline to diesel lowers the flash point of the blend to less than the minimum stated in the EN 590 standard.

OME$_1$ is easily synthesized from methanol [57]. Its combustion properties have thus been investigated by various researchers. Its physico-chemical properties require modifications of the current injection system or fuel distribution infrastructure when used as a fuel or a fuel additive. To circumvent these drawbacks, blend of OME$_1$ with various additives have been reported in the scientific and patent literature. E. Jacob patented a fuel containing OME$_1$ and 3–20 wt% of polyethylene glycol dimethyl ether (molecular weight of 500 or 1000 g/mol) [58]. Interestingly, the author also dissolved OME$_4$ or OME$_{6–10}$ in OME$_1$ to increase viscosity and cetane numbers in some embodiments of the patent. Feiling et al. compared emission characteristics of OME$_1$ with 3% long-chain polyethers (OME$_{1b}$) and a conventional diesel fuel (with up to 7 vol% FAME) using a single-cylinder engine at various loads [8]. At low (3 bar pressure mean indicator = p$_{mi}$) and high loads (7 bar p$_{mi}$), they recorded a twenty- and fortyfold particle number decrease, respectively, compared to conventional diesel fuel. According to the
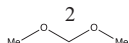
authors, the high temperature in the combustion chamber at high load favored the re-oxidation of soot. Additionally, OME$_1$ exhibited a soot-free combustion (particulate matter concentration below the device detection limit of 0.01–1 mg/m^3).

Finally, Härtl et al. investigated various oxygenated fuels and identified OME as the most effective for soot reduction [52,56]. Combustion and emissions of various OME blend were tested in a single-cylinder engine: OME$_{3–6}$, OME$_{1b}$ and OME$_{1a}$ (3 wt% of SYNALOX^{TM} 40-D700 and 3 wt% of polyethylene glycol dimethyl ether with a molecular weight of 1000 g/mol). The engine fuel system was also modified to use OME. During engine testing with a diesel oxidation catalyst (DOC) as sole after-treatment component, they demonstrated that the soot-NO$_x$ trade-off totally disappeared even at stoichiometric combustion. Furthermore, they verified that no formaldehyde emission occurred. However, they recorded methane emissions near stoichiometric condition that were not converted by the DOC. Methane emissions are believed to be due to an increase in methyl radical formation and their subsequent reaction with hydrogen radicals during combustion near stoichiometric condition.

3. Synthesis routes for the production of OME

OME are produced by reacting a methyl-end group provider with an oxymethylene group provider under acidic conditions. They can also be produced using a bi-functional catalyst combining redox and acidic properties with one reactant containing both moieties. Methanol, DME and OME$_1$ have been reported in the literature as the sources of the methyl end group. Different sources of monomeric formaldehyde have been reported, i.e. in liquid form as aqueous formaldehyde, in gaseous form as DME or in solid form as trioxane (TRI) and paraformaldehyde (PF). TRI, $C_3H_6O_3$, is a white crystalline solid with a melting point of 62 °C and boiling point

Table 2
Combination of reactants used for the synthesis of OME in the scientific literature.[a]

			capping source		
			1 Me——OH	2 Me-O-O-Me	3 Me-O-Me
Monomer source	=O	A	Zhang [65,66], Schmitz [67,68]	–	–
	(1,3,5-trioxane)	B	Zhao [69], Li H. [70], Deng [71], Fang [72], Wang [73]	Burger [47,74], Wang [75], Zhang [76], Wu Q. [77,78], Fu [79], Li [80], Wu J. [81], Wu Y. [78]	–
	HO(CH2O)nH	C	Oestreich [82]	Arvidson [83], Zheng [40,84,85], Li [86], Shi [51]	–
	Me-O-Me	D	–	–	Zhang [87,88]

[a] Includes studies where OME_n with more than one oxymethylene group were produced.

of 115 °C. This cyclic ether decomposes under acidic conditions to anhydrous formaldehyde according to Reaction (6). It is produced from concentrated aqueous formaldehyde solution with low conversion by acid-catalyzed ring formation, followed by a separation step composed of several distillation columns or a combination of distillation and solvent-extraction steps [59]. Xia et al. incorporated TRI production in their OME synthesis process in order to use the same extraction solvent [60].

PF or polyoxymethylene glycol, $HO\text{-}(CH_2O)_n\text{-}H$ with n = 8–100, is a short polymer composed of oxymethylene moieties. It is produced by concentration of aqueous formaldehyde under vacuum. PF powder decomposes to formaldehyde upon heating at temperature from 120 to 170 °C [61]. It depolymerizes in an acid-catalyzed reaction to formaldehyde in water according to the following reaction:
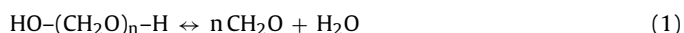
$$HO\text{–}(CH_2O)_n\text{–}H \leftrightarrow n\,CH_2O + H_2O \tag{1}$$

Finally, liquid and gaseous monomeric formaldehyde readily polymerizes at room temperature [61]. Dissolved in water, it polymerizes to form a distribution of poly(oxymethylene) glycols (PGs, $HO\text{-}(CH_2O)_n\text{-}H$) according to reactions (2) and (3) [62–64]. It also reacts with methanol to produce hemiformals (HFs, $CH_3\text{-}(O\text{-}CH_2)_n\text{-}OH$) based on Eqs. (4)–(5). These reactions do not require acid as catalyst and the equilibrium is far on the product side. Therefore, less than 0.1% formaldehyde is found in monomeric form in aqueous solution [61]. Due to its high reactivity, it is commercially available as formalin, an aqueous solution containing 37–55 wt% formaldehyde. Its methanol content is usually between 10–15% which inhibits the formation of insoluble polymers [61].

$$H_2O + CH_2O \leftrightarrow MG_1 \tag{2}$$

$$MG_n + CH_2O \leftrightarrow MG_{n+1} \tag{3}$$

$$CH_3OH + CH_2O \leftrightarrow HF_1 \tag{4}$$

$$HF_n + CH_2O \leftrightarrow HF_{n+1}(n > 1) \tag{5}$$

3.1. Synthesis routes

Three routes to synthesize OME can be identified in literature. These routes are used to classify the combinable reactants, yielding the desired OME (Table 2).

3.1.1. Anhydrous synthesis of OME [B2]

The reactants used in the anhydrous route are TRI with OME_1. OME_1 reacts with CH_2O units provided by the reversible reaction

(6). The OME synthesis with OME_1 and TRI follows these reversible reactions:

$$TRI \leftrightarrow 3CH_2O \tag{6}$$

$$OME_1 + CH_2O \leftrightarrow OME_2 \tag{7}$$

$$OME_n + CH_2O \leftrightarrow OME_{n+1}(n > 1) \tag{8}$$
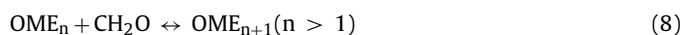
Anhydrous monomeric CH_2O should react with OME_1 in quantitative yield to OME_n. This reaction has however not yet been documented in the literature.

Usage of PF as monomeric formaldehyde provider implies water production according to Reaction (1) in proportion depending on the average PF chain length and the formation of hemiformals as side products.

3.1.2. Aqueous synthesis of OME [A1, A2, B1, C1]

Using methanol as the capping source leads to the production of water in stoichiometric amount. Under acidic conditions, it reacts with formaldehyde from aqueous or anhydrous sources according to the global reaction Eq. (9). A liquid–liquid equilibrium model was developed to predict the behavior of ternary system composed of water, methanol and OME [89].

$$2CH_3OH + nCH_2O \leftrightarrow OME_n + H_2O(n > 1) \tag{9}$$
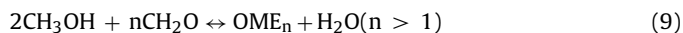
3.1.3. Selective, one-step oxidation of methanol to OME [1,D3]

OME_1 is usually produced from methanol in two consecutive steps: (i) gas-phase (oxi-)dehydrogenation of an excess of methanol over Ag catalysts to produce a mixture of formaldehyde, methanol and water followed by (ii) liquid-phase, acid-catalyzed condensation of methanol and formaldehyde. Relatively high yield can be achieved with this synthesis strategy [57]. There has been a recent focus on the synthesis of OME, mostly OME_1, through direct, one-step selective oxidation of methanol or DME over a bi-functional catalyst combining acidic and redox properties [12,88,90–94]. The recent review of Thavornprasert and al. [95] summarizes the research conducted on the one-pot synthesis of OME_1 from methanol. The first one-step OME synthesis process from methanol using oxygen as oxidant has been published by Yu et al. [35] in their patent application from 2010. They used a fixed bed continuous synthesis process. Zhang et al. investigated OME synthesis, notably OME_1 and OME_2, from DME on various catalysts [87,88,96].
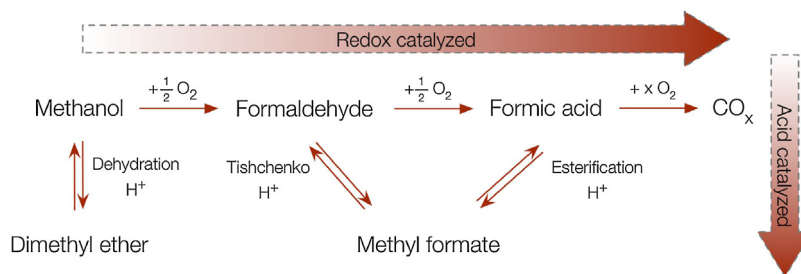
Fig. 4. Side reactions during OME synthesis adapted from ref. [74,95,97].
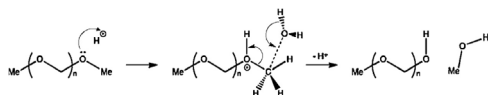
Fig. 5. Hydrolysis of OME under acidic conditions.

3.2. Side reactions during OME synthesis

OME preparation is subjected to several side reactions, presented in Fig. 4, that decrease the overall yield. Dimethyl ether is produced via methanol dehydration in an acidic environment [74,97,98]. Likewise, methyl formate is produced by the Tishchenko reaction from formaldehyde [6,73]. Formaldehyde or methanol can be oxidized to formic acid and can decompose to carbon monoxide or carbon dioxide [97,98]. Methyl formate is also produced via esterification of formic acid. The hydrolysis of OME with water is another important side reaction and is illustrated in Fig. 5 [40,65,74].

Water presence shifts the product distribution towards shorter chains. It also makes the separation process more tedious requiring extraction with non-polar solvents such as diesel. Various authors studied the influence of water on the reaction product distribution [40,67,82,99]. An addition of 10 wt% water decreases the amount of $OME_{>2}$ by 70.6%. Wang et al. also tested the influence of water on the synthesis of OME with methanol and TRI using graphene oxide as catalyst. They reported an 85% decrease in OME_{2-8} selectivity when using water as a solvent compared to methanol [73].

4. Catalysts

The synthesis of OME is described as an acid-catalyzed reaction. Different catalyst categories have been investigated in the patent and scientific literatures: liquid (Table 3) and heterogeneous (Table 4). Two criteria are used to evaluate the performance of a catalyst: its selectivity towards a range of OME of a certain chain length and the conversion of reactants. These criteria are difficult to compare from one study to another as the products of interest and the reactants vary. References cited here have reported the synthesis of OME_n with n > 1 except in the case of selective, one-step synthesis of OME_1.

4.1. Liquid catalysts

Mineral acids such as H_2SO_4, HCOOH, CF_3SO_3H have been reported in many patents as catalysts for the synthesis of OME [30,31,34,100]. There have been fewer reports in the scientific literature. Wang et al. tested various liquid catalysts containing carboxyl, carbonyl, hydroxyl and sulfonic groups [73]. Their results showed that the acidity of carboxyl, carbonyl and hydroxyl groups is not sufficient for efficient TRI decomposition and OME chain growth. Best results were obtained with catalysts containing a sulfonic acid functional group such as sulfuric acid, for which a TRI conversion of 72.2% and an OME_{2-8} selectivity of 19.3% was achieved. Shi et al. tested several rare earth metal compounds with sulfuric acid and identified lanthanum (La^{3+}/SO_4^{2-}) as an efficient co-catalyst [51].

Amongst the liquid acid catalysts, ionic liquids (ILs) have several advantages. They are powerful solvents with high tunability of solvent and acidic properties. Due to their low vapor pressure and high thermal stability, they are easier to separate and recycle [77]. They have been used for the synthesis of OME and several have been patented. Chen et al. filed several patent applications on methods for producing OME catalyzed by ILs using OME_1 or methanol with TRI under nitrogen pressure [101–103]. They disclosed their best performance with a quaternary phosphonium salt, namely triphenyl(propyl-3-sulfonyl) phosphonium trifluoromethanesulfonate ([PH-S][CF_3SO_3-]), with a TRI conversion of 90.3% and an OME_{3-8} selectivity of 42.6%, with methanol and TRI as reactants [101]. Superior OME_{3-8} selectivity of 52.4% was achieved later using OME_1 as capping source and 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ([IM-S][HSO_4^-]) as catalyst with a similar TRI conversion of 89.1% [102]. They also developed a continuous process using methanol or OME_1 and TRI with the same ILs [104]. They disclosed that their product stream contained 73.5% of OME_{3-5} after separation with a 93.1% single-pass conversion of TRI.

Xia et al. subsequently patented a method based on the same ILs catalysts for continuously producing OME using aqueous formaldehyde (50–60 wt%) and methanol in a two-steps process [60,105]. First, formaldehyde polymerizes to TRI, followed by an acetylation reaction to OME. They achieved a production of 200 mL/h of

Table 3
Liquid catalysts used for the synthesis of OME.

Catalysts (wt%)	Reactants (molar ratio)	T (K)	Time (h)	Conversion (%)/source	Selectivity (%) to OME_{x-y}	Ref.
Mineral acid						
H_2SO_4 (0.1)	OME_1 and PF (4:1)	373	1	68.6/PF	27.6 (3–4)	[107]
H_2SO_4 (0.27)	MeOH and TRI (2:1)	393	10	72.2/TRI	19.3 (2–8)	[73]
La^{3+}/SO_4^{2-} (1)	OME_1 and PF (1:1.6)	393	6	83.2/OME_1	50.73 (3–8)	[51]
CF_3SO_3H (0.01)	OME_1 and TRI (4:1)	373	40	undisclosed	22.5 (3–11)	[30]
Ionic liquids						
[PH-S][$CF_3SO_3^-$] (2.1)	MeOH and TRI (1.3:1)	393	4	90.3/TRI	42.6 (3–8)	[101]
[IM-S][HSO_4^-] (4.5)	OME_1 and TRI (1.1:1)	388	0.66	89.1/TRI	52.4 (3–8)	[102]
[PY-BS][HSO_4^-] (1.61)	OME_1 and TRI (3:1)	443	10	91.2/TRI	70.9 (3–8)	[77]

Table 4
Heterogeneous catalysts used for the synthesis of OME.

Catalysts (wt%)	Reactants (molar ratio)	T (K)	Time (h)	Conversion (%)/source	Selectivity (%) to OME_{x-y}	Ref.
Ion exchange resin						
A36 (4.2)	OME_1 and TRI (2:1)	323	0.33	93.5/TRI	31.5 (3–6)	[47]
NKC-9 (7.0)	OME_1 and PF (3:1)[a]	353	1.5	84.6/PF[a]	36.6 (3–5)	[84]
Dowex50Wx2 (1.0)	MeOH and PF (1:1.6)	353	0.023	undisclosed	29.3 (3–5)	[82]
Carbon material						
HS-C (undis.)	OME_1 and TRI (undis.)	323	48h	undisclosed	31.9 (3–7)	[109]
GO (5)	MeOH and TRI (2:1)	373	10h	92.8/TRI	30.9 (2–8)	[73]
Solid superacid						
$ZrO_2/\gamma\text{-}Al_2O_3$ (0.5 g)[b]	MeOH and aqu. FA (1:3)	393	0.013[c]	91.3/FA	23 (3–8)[d]	[65]
SO_4^{2-}/TiO_2 (1.0)	OME_1 and TRI (1:1)	353	1	89.5/TRI	54.8 (3–8)	[80]
SO_4^{2-}/Fe_2O_3 (1.5)[e]	MeOH and TRI (1.5:1)	403	2	81.9/TRI	23.3 (3–8)	[70]
Zeolite						
HMCM-22 (5)	OME_1 and TRI (1:2)	393	10	undisclosed	29.4 (3–8)	[69]
HZSM-5 (5)	OME_1 and TRI (2:1)	393	0.75	85.3/TRI	88.5 (2–8)	[81]
Other						
PVP-HPAs (2.3)	MeOH and TRI (2:1)	413	4	95.4/TRI	54.9 (2–5)	[72]
C10-AS-50 (7)	OME_1 and TRI (3:1)	378	2	92.6/TRI	53.5 (3–8)	[79]
Si-ILs (4)	OME_1 and TRI (3:1)	378	1	92/TRI	52 (3–8)	[78]
$Re\text{-}PW_{12}/TiO_2$ (1 mL)[f]	DME	513	0.0003s[c]	15.6/DME	60.0 (2)	[87]

[a] The author indicates a molar ratio of OME_1/CH_2O of 3:1 and a formaldehyde conversion of 84.6%. The mean chain length of PF and the method to produce the formaldehyde are not mentioned.

[b] Mass of catalyst in a fixed-bed reactor, molar ratio Zr/Al = 0.04.

[c] Experiments conducted in a continuous setup. Indicated time = residence time.

[d] Number taken from Fig. 7 in ref. [65].

[e] 6.4 wt% SO_4^{2-} on Fe_2O_3.

[f] 5 wt% Re and 20 wt% PW_{12} on TiO_2.

OME_{3-8} during 100 h from an aqueous formaldehyde solution (feed rate = 800 mL/h), which was converted to TRI with a feed rate of 130 mL/h followed by reaction with 112 mL/h of methanol. Catalytic performance of a series of Brønsted acid ILs with different alkenesulfonic acid groups was investigated by Wu et al. for the synthesis of OME with OME_1 and TRI [77]. They determined that a stronger Brønsted acidity improves this reaction with 1-(4-sulfonic acid) butylpyridinium hydrogen sulfate ([PY-BS][HSO_4^-]) as their best catalyst. Whereas the conversion of TRI was basically unaltered (<90%), the selectivity to OME_{3-8} varied significantly. They later studied the influence of ILs hydrophobicity on their catalytic performances for the synthesis of OME with OME_1 and TRI [106]. For this purpose, ILs with a carbon side-chain of varying length were synthesized and it showed that the hydrophobicity has only limited influence on the catalysts performance under their reaction conditions. While the conversion of TRI remained constant above 90%, the OME_{3-8} selectivity peaked at 57.85% for a carbon chain length of 6 corresponding to the lowest viscosity. However, they did not consider the potential change in acidity resulting from the modification of ILs side chains.

In summary, homogeneous liquid catalysts have inherent advantages in OME synthesis such as being uniformly distributed in the reaction mixture and having all their catalytic sites available for the reaction. However, they are difficult to separate. On the one hand, mineral acids are inexpensive but corrosive, harmful to the environment and they only exhibit little OME selectivity. On the other hand, ILs are expensive and exhibit slow substrate diffusion but they show better performance, especially better selectivity towards OME.

4.2. Heterogeneous catalysts

Ion-exchange resin catalysts combine some chemical benefits of homogeneous catalysis, i.e. their well-defined and uniform active sites, with the characteristic physical advantages of heterogeneous catalysis. They are even used in combination with homogeneous catalysts to further improve the activity and selectivity [108]. Therefore, they are often used as catalysts for the synthesis of OME.

However, the majority of the concerned literature studies focused only on their application, but few on the influence of the catalyst features. Arvidson et al. reported the usage of Amberlite® IR120 for reacting PF with OME_1 and identified LiBr as promoting co-catalyst [83]. Burger et al. compared Amberlyst® 36 (A36) and 46 (A46) for the production of OME [74]. They obtained between 1–2 wt% of the side products DME and methyl formate using A36 compared to a completely selective reaction when using A46. They suggested that side products are catalyzed by the sulfonated active sites in the catalyst micropores where formaldehyde may accumulate. A46 features no active sites in the micropores and hence produces less side products.

Performance of several ion-exchange resins (NKC-9, D001-CC, D72) with sulfonic acid groups were investigated by Zheng et al. for the synthesis of OME from OME_1 and PF [84]. NKC-9 exhibited the best catalytic performance with 84.6% formaldehyde conversion and 36.6% OME_{3-5} selectivity. Higher surface area, higher exchange capacity and larger pore volume have led to the higher performance of NKC-9. Because all these parameters vary for NKC-9, it is difficult to study the influence of each individual parameter. However, D001-CC and D72 have similar BET surface area and exchange capacity and differ only with respect to their pore volume, which is higher for D72 resulting in a twofold increase in formaldehyde conversion and an enhanced selectivity compared to D001-CC.

Using ion exchange resins as catalysts include diffusion from the bulk to the particle as well as potential subsequent diffusion of the molecules inside the micropores to the active sites depending on the characteristics of the resins.

Zheng et al. investigated the limitations of the internal and external mass transfer by varying the particulate diameter and stirring speed, respectively, with a NKC-9 catalyst [40]. They did not observe internal mass transfer limitation for particle diameters smaller than 1 mm. A stirring speed higher than 300 rpm was necessary to eliminate external mass transfer effect. The reusability of the resins was tested by various groups [75,84]. In general, no major change in the activity of the resins was observed after several reuses. Oestreich et al. observed a 10% decrease in reactants con-

version with no change in selectivity after using the Dowex50Wx2 resin continuously for 17 days [82]. The drawbacks of ion exchange resins are their low thermal stability and the leaching of active species into the bulk of the solutions when using polar solvents. A continuous process that used an ion exchange resin to produce OME was patented using PF or TRI and OME_1 as reactants [110]. It claimed to obtain a product stream with a 53.27 wt% of OME_{2-7}.

Compared to acidic resins, solid acid carbons do not swell and exhibit higher thermal stability. Shen and co-workers developed an acidic carbon catalyst containing sulfonic acid groups (HS-C) from the carbonization and sulfonation of a phenolic-like structure [111]. It was used for the synthesis of OME from OME_1 and TRI [109]. The phenolic-like structure was obtained by hydrolyzation of glucose to hydroxymethylfurfural and subsequent reaction with a phenol compound. They obtained an OME_{3-7} selectivity of 31.9%. Wang et al. used graphene oxide (GO) with methanol and TRI, obtaining a TRI conversion of 92.8% and an OME_{2-8} selectivity of 30.9% [73]. Since GO contains various oxygen-containing functionalities such as carboxyl, hydroxyl, carbonyl and sulfonic groups, investigating the effect of each functional group on catalyst activity was important. Selective removal of carbonyl, carboxyl or hydroxyl groups resulted in 18% less TRI and methanol conversion while removal of sulfonic groups resulted in 57% less conversion. OME_{2-8} selectivity decreased similarly when all functional groups were eliminated with an average of 72% decrease. It became apparent that sulfonic, hydroxyl and carboxyl groups are all crucial for the catalytic performance of GO, especially the sulfonic group for TRI decomposition. Despite its good catalytic performance, GO reusability is limited since a decrease of 8% and 47% in TRI conversion and OME_{2-8} selectivity, respectively, was observed after five cycles.

Solid superacid catalysts were also reported to be active in OME synthesis process. Zhang et al. used a zirconia on alumina $(ZrO_2/\gamma-Al_2O_3)$ catalyst for OME synthesis from formaldehyde and methanol [65]. Addition of ZrO_2 to unmodified alumina changes its acidity with an increment of its medium and strong acid centers. They tested the effect of the catalyst Zr/Al molar ratio on the reaction in a fixed bed reactor. Increasing the Zr/Al ratio led to increased methanol conversion with an optimal selectivity at 0.04. They recorded 91.3% formaldehyde conversion and 23% OME_{3-8} selectivity. The catalyst proved to be stable during reaction over 500 h without decrease in conversion or selectivity. Chungu's group tested the catalytic performance of various super solid acids for the synthesis of OME. Sulfated titania $(SO_4{}^{2-}/TiO_2)$ exhibited 89.5% TRI conversion and 54.8% OME_{3-8} selectivity using OME_1 and TRI as the reactants [80]. They also used sulfated iron silica $(SO_4{}^{2-}/Fe_2O_3\text{-}SiO_2)$ with various pre-treatment methods and amounts of silica [70]. They studied the influence of number, ratio and density of Lewis and Brønsted acid sites on catalytic activity. The best sample was a sulfated iron catalyst with no silica that had the highest acidity, the highest ratio of Brønsted to Lewis acid sites, and the highest acid site density. It led to 81.9% TRI conversion and 23.3% OME_{3-8} selectivity.

Nearly complete conversion of TRI and 54.9% OME_{2-5} selectivity was reported by Fang et al. with polyvinylpyrrolidone-stabilized phosphotungstic-acid (PVP-HPW) in a PVP/HPW molar ratio of 0.25:1 [72]. They varied the PVP/HPW ratio to tune the acidity.

In a recent publication, ILs supported on silica gel (Si-ILs) were used to combine the efficiency of ILs (3-sulfobutyl-1-(3-propyltriethoxysilane) imidazolium) with the usability of heterogeneous catalysts [78]. Si-ILs have better catalytic activity than their unsupported counterpart with reported TRI conversion and OME_{3-8} selectivity of 92% and 52%, respectively. However, they exhibited limited reusability with a loss of 22.8% of its grafted catalytic material after six runs and one regeneration. This loss led to a decrease of 45% and 42% of the TRI conversion and the OME_{3-8} selectivity, respectively.

One of the interesting features of zeolites as catalysts is their tunable acidity by the adjustment of their Si/Al ratio. Their Brønsted and Lewis acidity arise from the bridged linkage of Si-(OH)-Al and Al defects, respectively. Zhao et al. investigated the activity of the zeolites HY, HZSM-5, HMCM-22 and Hβ on the product distribution of OME with methanol and TRI as the reactants [69]. HMCM-22 showed the highest OME_{3-8} selectivity due to its larger number of acid sites compared to other tested zeolites. They determined that a Si/Al ratio of 200 generates the highest selectivity for HMCM-22. However, they did not control the effect of the Si/Al ratio on the conversion of reactants. Wu et al. also studied the influence of the Si/Al ratio on the conversion of TRI or OME_1 and the selectivity towards OME_{2-8} using HZSM-5 as catalyst [81]. They found 580 as the optimum Si/Al ratio. By means of pyridine adsorption and FTIR spectroscopy, they calculated that an increase of the ratio diminishes the amount of acid sites, most notably Lewis acid sites. The ratio of Brønsted to Lewis acid sites increases from 0.9 to 5.8 with an increase in the Si/Al molar ratio from 56 to 560, corresponding also to a decrease from 47.3 to 0.2 wt% of methyl formate selectivity. At too high Si/Al ratio, the catalytic activity started to deteriorate severely.

Additionally, Yu et al. impregnated an acidic molecular sieve with two metal oxides and used this catalyst in a one-step OME synthesis process from methanol using air as the oxidant [35]. The catalyst was composed of 60–90 wt% of zeolite Y or ZSM-5, 2–20 wt% molybdenum oxide and 0.2–10% iron oxide. They claimed that they have achieved a single-pass methanol conversion of 96–98%, similar to the industrial formaldehyde production process [61]. They also claimed to obtain 34% $OME_{>2}$ selectivity, the rest of the product being methanol, formaldehyde, OME_1, water, DME and CO_x.

Super-microporous aluminosilicates $(C_{10}\text{-AS-50})$ were prepared by Fu et al. for the synthesis of OME using OME_1 and TRI as reactants [79]. Super-microporous materials have a pore size range between those of microporous zeolites and ordered mesoporous materials. They achieved 92.6% TRI conversion and 53.5% OME_{3-8} selectivity.

4.3. Catalyst for direct gas-phase synthesis of OME

The majority of research on the direct gas-phase synthesis of OME involves the selective oxidation of methanol over heterogeneous catalysts. The review of Thavornprasert et al. offers detailed information on the catalysts used for OME_1 one-step synthesis [98]. Various metal oxides have been reported such as molybdenum-, ruthenium-, rhenium- or vanadium oxide. The highest catalyst activity reported in the literature was claimed by Gornay et al. using an FeMo-based catalyst, traditionally used for formaldehyde synthesis from methanol under methanol-lean and air-rich conditions [112]. However, using this catalyst in OME synthesis under methanol-rich conditions resulted in 56% methanol conversion and 90% OME_1 selectivity. Increased OME_1 yield was also obtained by Lu et al. by impregnation of V_2O_5/TiO_2 with H_2SO_4 [91]. The H_2SO_4-modified catalyst reached a methanol conversion and OME_1 selectivity of 49.0% and 93.0%, respectively. Additionally, a gas-phase DME conversion of 15.6% and an OME_2 selectivity of 60.0% was reported using rhenium oxide (Re_2O_7) modified $H_3PW_{12}O_{40}$ supported on TiO_2 $(Re\text{-}PW_{12}/TiO_2)$ [87]. $Re\text{-}PW_{12}$ was also supported on carbon nanotubes but higher OME yields were not achieved. In summary, for OME_1 one-step synthesis oxidizing and acidic properties of actives sites are of crucial importance to maximize OME_1 yield, but deriving general conclusions is difficult. However, the provided data at least suggest that redox and acid sites of the right strength should likewise be in close vicinity.
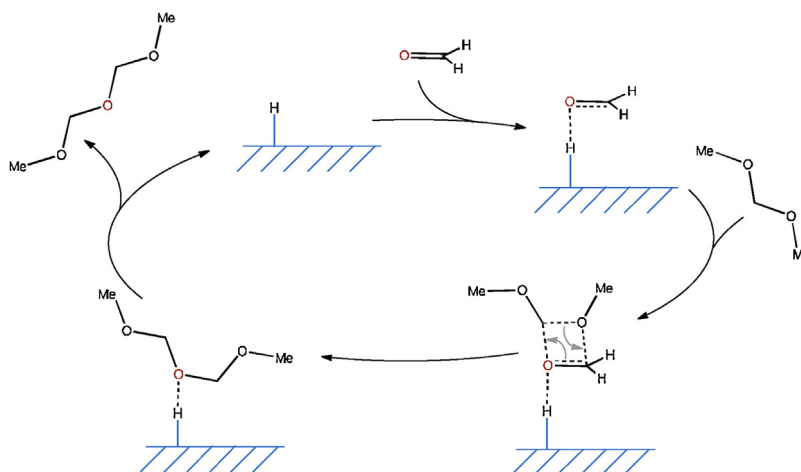
Fig. 6. Eley-Rideal reaction scheme representing the sequential addition mechanism for the synthesis of OME$_2$ from OME$_1$ and formaldehyde on an acidic surface where H represent an acidic active site on a surface based on Wu et al. [81].

5. Reaction mechanisms

5.1. Decomposition of formaldehyde sources

All OME syntheses require a methyl-end group provider and an oxymethylene group provider. PF or TRI are often used as sources of the oxymethylene group, which implies two conceivable reaction pathways in OME synthesis. The first is a reaction without prior TRI decomposition or with PF partial decomposition. The second is a complete decomposition of PF or TRI before the reaction. In theory, the reaction of OME$_1$ with undecomposed TRI would lead to a higher OME$_4$ selectivity than experimentally reported in the literature. However, the formation of such a preferential chain length is unknown to the best of our knowledge. The same is valid for PF. Therefore, there is a general agreement that TRI or PF should decompose first before participating in the OME synthesis reaction. Using density functional theory (DFT), Wang et al. calculated that TRI observes a two-step decomposition mechanism on SO$_3$H-ILs prior to reaction with methanol or OME$_1$ [113]. First, TRI is protonated causing ring opening and formation of a linear trioxymethylene intermediate. Subsequently, the intermediate form decomposes to produce three formaldehyde monomers. In contrast to TRI, PF containing three oxymethylene moieties decompose in a one-step mechanism before reaction with methanol or OME$_1$. PF simultaneously gets protonated, releases a water molecule and decomposes. For longer PF molecules, however, an unzipping mechanism is reported in which formaldehyde monomers are produced one by one [20,51,84]. The availability of monomeric formaldehyde from the decomposition of its precursor compounds probably plays a significant role on the product distribution, side product formation and reaction kinetics.

5.2. Chain growth mechanisms

Two reactions mechanisms have been reported in the literature to describe the chain growth of OME: (i) a sequential addition mechanism [40,71,81,84,106] and (ii) an initiation, growth and termination (IGT) mechanism [68,70,72,78,84,113]. The reaction mechanism followed seems to depend on the phase, reactants and catalyst.

On the one hand, OME are produced via the sequential addition mechanism in liquid, anhydrous phase with any acid catalysts except ILs. During sequential addition, formaldehyde monomers are inserted into OME$_1$ according to Eqs. (7)–(8). Monomeric formaldehyde is provided by TRI or PF decompo-

sition. Various elementary steps have been reported in the literature. Arvidson et al. first suggested that protonated formaldehyde is inserted into OME with lithium bromide as a promoter using an Amberlite IR120 ion-exchange resin catalyst [83]. Burger et al. subsequently built a model based on a customized Langmuir−Hinshelwood−Hogan−Watson mechanism in which monomeric formaldehyde and OME chemisorb before a surface addition reaction occurs [74]. They did not detail a mechanism on the OME chemisorption. More recently, various authors suggested an Eley-Rideal mechanism where chemisorbed, monomeric formaldehyde reacts with OME in the liquid phase on sulfated active sites in an NKC-9 ion-exchange resin and on Brønsted acid sites of a HZSM-5 zeolite [40,81,84]. Fig. 6 depicts the proposed reaction mechanism [81]. Finally, Shi et al. suggested a homogeneous reaction pathway for the synthesis of OME from OME$_1$ and TRI with La^{3+}/SO$_4^{2-}$ catalyst [51].

On the other hand, we suggest that OME synthesis follows an initiation, growth and termination (IGT) chain growth mechanism in aqueous phase or when using ILs. The main difference to the sequential addition mechanism is that the IGT mechanism involves an intermediate during the growth phase. Two reaction intermediates have been reported in the literature: carbocations and hemiformals. Hemiformals (HFs, CH$_3$-(O-CH$_2$)$_n$-OH) are intermediates produced from methanol reacting with formaldehyde according to Eqs. (4)–(5), which describe the initiation and chain growth reactions. They can react under acidic conditions with methanol to produce OME through acetalization (10) and a combination reaction (11), which are the termination reactions for HFs chain growth.

$$HF_n + CH_3OH \leftrightarrow OME_n + H_2O(n \geq 1) \tag{10}$$

$$HF_n + HF_m \leftrightarrow OME_{n+m} + H_2O(n, m \geq 1) \tag{11}$$
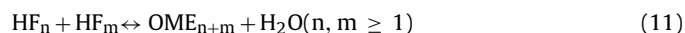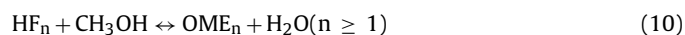
To the best of our knowledge, reaction (11) was only suggested by Zhang et al. in their kinetic model [65]. It describes OME synthesis through an HF condensation reaction mechanism. However, only reactions of HFs with HF$_1$ were considered.

Carbocations (C$_n^+$, CH$_3$-(O-CH$_2$)$_{n-1}$-O-CH$_2^+$, n $\geq$ 1) are produced as shown in Fig. 7 through dehydration of HFs or the loss of a methanol group from an OME. They require stabilization that can be provided by the solvent or IL catalyst. Their presence in other polar, protic solvent, i.e. water, methanol has not been confirmed. Their chain growth mechanism is similar to HFs formation with an oxocarbenium ion as the active center which reacts according to Eq. (12). Eq. (13) describes the termination reaction as well as the ini-

Fig. 7. Carbocation initiation from HF_s and OME_1.

tiation reaction in backward direction. DFT calculations conducted with SO_3H-ILs as the catalyst suggest a carbocation mechanism for OME_1 and a hemiformal-carbocation pathway for methanol with monomeric formaldehyde provided by TRI or PF decomposition [113]. In contradiction, OME_1 and TRI were suggested to follow a sequential addition mechanism with ILs catalyst containing a sulfonic acid group by Wu et al. [106].

$$C_n^+ + CH_2O \leftrightarrow C_{n+1}^+ \qquad (12)$$

$$C_n^+ + MeOH \leftrightarrow OME_n \qquad (13)$$

Reaction mechanisms involved in the direct, one-step selective synthesis of OME differs from chain growth reactions. According to Tatibouët et al., OME_1 one-pot synthesis from methanol over metal oxide catalysts occurs according to the following mechanism [92]. First, methanol is strongly adsorbed on the catalyst surface or forms a methoxy surface group, which is further oxidized to an adsorbed formaldehyde or dioxomethylene specie. These intermediates then react with methanol to form surface-bound hemimethylal species (CH_3OCH_2O-). Fi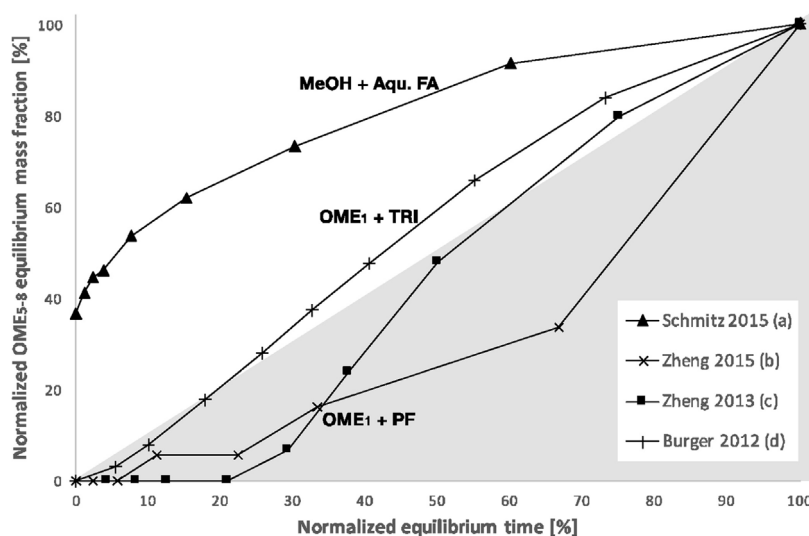nally, another methanol molecule reacts with the hemimethylal specie to form OME_1. The authors suggested that on the surface of unsupported V_2O_5, methanol could be activated through homolytic C—H bond breaking to form highly reactive radical species $\bullet CH_2OH$. The latter would then react with adsorbed methanol or methoxy species to form HF_1 adsorbed via the oxygen atom of the oxymethyl group. The redox and acid properties of the catalyst are thus key to guide the reaction towards the desired pathway.

Another study on OME_1 and methyl formate formation was conducted by Liu et al. over RuO_2 on various supports [93]. According to them, methanol oxy-dehydrogenation to formaldehyde requires C—H activation during which lattice oxygen abstracts the hydrogen atom to subsequently form water. Dissociative chemisorption of oxygen from the feed completes the Mars-van Krevelen redox cycle by filling the oxygen vacancies. OME_1 is produced via secondary reactions on the acid sites of Al_2O_3 or SiO_2. Methyl formate will be preferentially formed if SnO_2, ZrO_2 or TiO_2 containing redox and amphoteric sites are used as supports instead.

The direct, selective OME_1 synthesis from DME was suggested to start with the irreversible DME dissociation via concerted reactions with lattice oxygen and a metal center to form two methoxy species [94,114]. The latter undergoes subsequent reaction with hydroxyl groups to form methanol. They also form formaldehyde by hydrogen transfer that regenerates the hydroxyl groups. The mechanism of subsequent OME_1 formation has not been described but can be assumed similar to what has been explained before. No mechanism was yet proposed for the synthesis of larger OME in the gas phase except by Zhang et al. They suggested a C—H bond cleavage of OME_1 to form a $CH_3OCH_2OCH_2$— group that reacts with a methoxy group to form OME_2 [87].

5.3. Simultaneous vs. sequential OME formation

The OME synthesis follows two different types of reaction pathways based on the literature, which is deducible from the shape of the product distributions plotted in Fig. 8. In one type of reaction pathway, longer chains are not detected at the start of the reaction, whereas in the other type, chains of all lengths are observed right

from the beginning. OME synthesis follows thus either a sequential or simultaneous formation pathway.

Schmitz et al. obtained simultaneous OME formation with methanol and aqueous formaldehyde [67,68]. According to them, the reactions for the formation of HFs (4) and their growth (5) are fast compared to termination reactions—acetalization (10) or combination (11). HFs would thus have a product distribution in pre-equilibrium and would form OME of various chain lengths when the termination reactions start. In comparison, various authors who worked on OME_1 and TRI or PF conversion, i.e. under anhydrous synthesis conditions, have reported sequential formation that corroborates with the sequential addition mechanism for the synthesis of OME [40,74,84]. Additionally, Fig. 8 suggests that longer OME are more readily obtained when using TRI as the source of monomeric formaldehyde instead of PF. The slower release of monomeric formaldehyde due to PF depolymerization mechanism could explain this observation since monomeric formaldehyde is not available to react during OME synthesis.

5.4. Molecular size distribution

Studies with different catalysts and reactant types reported that the molecular size distribution of OME under equilibrium conditions follows the Schulz-Flory (SF) distribution [40,81,109,113]. One study even demonstrated that it is also applicable to describe the transient product distribution [85]. SF distribution is generally used in polymer chemistry. It entails that the product distribution is purely statistical and that the reactivity of OME is independent of the chain length. It is determined by the probability of chain growth on a catalyst [115]:

$$x_n = (1 - \alpha) \cdot \alpha^{(n-1)} \text{ with} (n > 0) \qquad (14)$$

Where n, x_n and α are the chain length, the molar fraction of products with a chain length of n and the probability of chain growth, respectively. Larger α refers to the larger average molecular weight of the produced OME. Compared to polymer chemistry, relatively low values of α have been reported, which translates into a OME product distribution containing mainly low molecular weight molecules.

Similarly, SF distribution predicts Fischer-Tropsch (FT) product distribution [115]. There are, however, some deviations for FT reactions, notably a higher and lower selectivity for C_1 and C_2, respectively. No study has been reported until now that systematically investigates deviations from the SF distribution for OME. However, first attempts were made to influence selectivity. Fu et al. used different porous materials as catalysts to investigated the effect of pore size on selectivity using the catalysts USY-1, USY-3 (60) (micropores), C_{10}-AS-50 (supermicropores = between micropores and mesopores) and C_{16}-Al-SBA-1 (mesopores) for OME synthesis [79]. With C_{10}-AS-50, they managed to increase the OME_{3-8} selectivity by 4.6% and 2.9% compared to microporous and mesoporous materials, respectively. The catalyst had a similar number of acid sites and comparable acid strength. They reasoned that the selectivity achieved is matching between the pore dimension and the calculated size of the different OME leading to a partially restricted diffusion into the super-microporous materials.

5.5. Kinetic models

Kinetic investigation is a necessary step for reactor design and a tool for determining or confirming the reaction mechanism. Several kinetic investigations of OME synthesis have been reported in the literature as shown in Table 5. These kinetic models were built using reaction data from different catalysts, reactant types and reaction conditions. Each of them also have different underlying assump-

Fig. 8. Normalized OME$_{5-8}$ product weight fraction as a function of normalized reaction time to equilibrium. The reactions conditions are: (a) Schmitz 2015, T = 90 °C, MeOH/FA = 1:1.16, 12.73 g A46. (b) Zheng 2015, T = 60 °C, OME$_1$/PF = 2:1, 5 wt% NKC-9. (c) Zheng 2013, T = 80 °C, OME$_1$/PF 3:1, 1.0 wt% NKC-9. (d) Burger 2012, T = 50 °C, OME$_1$/TRI = 2.42:1, 0.91 wt% A46. Data points were connected for the sake of clarity.

Table 5
Available kinetic models for the synthesis of OME.

Model	Catalyst	Reactants	Reactor type	Ref.
Modified LHHW[a]	Ion exchange resin A46	OME$_1$ & TRI	Batch	[74]
Pseudo-homogeneous	Ion exchange resin A46	MeOH & FA	Batch	[68]
Power law	Ion exchange resin	MeOH & FA	Plug Flow	[66]
Power law	Ion exchange resins NKC-9	OME$_1$ & PF	Batch	[40]
Power law	ZrO$_2$/TiO$_2$	MeOH & FA	Plug Flow	[65]

[a] LHHW = Langmuir–Hinshelwood–Hougen–Watson.

tions. It is therefore difficult to compare the calculated parameters, e.g. activation energies and pre-exponential factors.

Burger et al. first modelled the reaction of TRI and OME$_1$ over the acidic ion-exchange resin A46 [74]. They used a modified Langmuir–Hinshelwood–Hougen–Watson reaction mechanism in which they assumed fast, at-equilibrium reactions of adsorbed species on the catalyst surface and rate-limiting sorption processes. They also assumed, based on the similar properties of OME of different chain length, that the adsorption and desorption rate constants are independent of the chain length. Furthermore, they assumed that all surface reaction equilibrium constants are independent of the length.

Their kinetic model describes closely the recorded concentrations of products, from different starting reactant concentrations. However, they considered that the decomposition of TRI requires three active sites to hold the protonated formaldehyde. Hence, they did not consider that any monomeric formaldehyde was in the reaction mixture. This is contrary to the DFT calculations that highlighted a TRI decomposition into three formaldehyde monomers, which subsequently interact with the sulfonic group of the ILs [113].

Zheng et al. built a kinetic model based on a sequential, reversible addition mechanism using OME$_1$ and PF with 5 wt% of NKC-9 ion exchange resin [40]. They assumed a first-order kinetics with respect to each reactant. They thus obtained second-order kinetics for the forward addition and a first-order kinetic for the reverse reaction. The model globally follows concentration trends but was not able to describe the transient period. This can be particularly observed from the differences between the model predictions and the experimental data for OME$_{2-3}$ concentrations. The following assumptions were made in their study: (i) the concentration of formaldehyde was considered constant during the reaction,

(ii) the forward and reverse sequential addition constants were considered independent of the chain length, (iii) chain lengths of maximum 6 CH$_2$O unit were considered, (iv) a constant volume with average density of 1.0 g cm^{-3} was assumed. Water and methanol were not considered in the model, since the maximum calculated amount of water in the mixture was 0.7 wt% and the measured amount of methanol was less than 1 wt%.

Zhang et al. modelled OME synthesis in a continuous setup [65,66]. Using methanol and aqueous formaldehyde with an ion-exchange resin as catalyst, they built a model based on a sequential addition mechanism even though their reaction was in aqueous conditions. They considered that OME$_1$ was first produced by Reaction (10) and grew through subsequent sequential addition of monomeric formaldehyde. However, only fair agreement between model prediction and experimental data could be achieved. They also built a second model of OME synthesis from methanol and aqueous formaldehyde using ZrO$_2$/TiO$_2$ as catalyst [65]. In contrast to their other model, they applied an IGT chain growth mechanism with HFs as intermediates. They considered: (i) initiation by reaction (4) and the reverse of reaction (10); (ii) termination of HF$_s$ only through combination reaction (11) of HFs with HF$_1$. Although they did not include reactions between monomeric formaldehyde and HFs, a good data-model fit with r^2 > 0.99 has been achieved.

Schmitz et al. [68] used a pseudo-homogeneous approach to model the reactions of methanol and aqueous formaldehyde with an A46 ion exchange resin. They assumed that the active sites of the resin are homogeneously distributed and freely accessible in the reaction mixture. Their kinetic model accounted for formaldehyde forming MGs and HFs in fast pre-equilibrium reactions. OME formation was considered to proceed via sequential growth addition and IGT chain growth mechanism. It was found that when the reaction was conducted without OME$_1$, the model without the sequential

addition correctly predicts the experimental data. When OME_1 was fed along with methanol and aqueous formaldehyde, only the combined model described properly the experimental data. They assumed that acetalization and sequential addition reaction rates as well as the growth constant were independent of the chain length. They accounted for limited chain length of 10 for HFs and PGs.

A reliable model for the synthesis of OME must predict the evolution of the concentrations inside the reactor when recycled products are being fed together with reactants. Burger et al. tried a pseudo-homogeneous model which fitted the experimental data except when OME_2 and OME_1 were fed into the reactor [74]. Schmitz et al. faced similar issues and changed their model by including a growth reaction to accurately predict product and reactant compositions [68]. The model presented by Zheng et al. seems to accurately predict the results when OME_{5-6} are fed into the reacting mixture [40]. However, the test experiments with OME_5 and OME_6 were conducted with an unrealistically high concentration of approximately 1 mol/L and 0.25 mol/L, respectively, compared to the expected concentration of these components during OME synthesis after 100 min. It would be of high interest to test the model-data fit with a feed of OME_2. Other models did not confirm their calculations when recycling was considered [65,66].

6. Conclusion and outlook

OME are appealing synthetic, functionalized oxygenated fuels. Their physico-chemical properties allow their usage with slight modifications of the engine or the distribution infrastructure. They prevent hazardous exhaust gas emissions at the origin and are complementary with current catalytic exhaust gas treatment methods. With no C-to-C bonds and thanks to the formation of hydroxyl radicals during combustion, they exhibit strongly reduced soot particle formation, allowing subsequent higher EGR to reduce NO_x emissions. They are produced from syngas, via methanol as versatile bulk chemical. If produced from renewable sources, it also has a neutral CO_2 footprint.

However, current liquid-phase processes involve production of costly intermediates such as OME_1 or TRI. Besides, OME product distribution was found to follow the SF distribution. The selective synthesis of OME_{3-5} is therefore more onerous. Current research efforts focus on simplifying the existing processes by using fewer steps and simpler reactants such as formaldehyde and methanol. However, a systematic study on the economics of the different OME synthesis is missing. Selective, direct oxidation of methanol or DME is an attractive alternative to liquid-phase synthesis but has yet to demonstrate viable prospects. Several catalyst classes are described which promote the acid synthesis of OME. Comparison of their performance is arduous because the current studies involve different reaction conditions, reactants and product of interest. Some are reported to favor the production of the desired product range. Moreover, little is known on the reaction mechanism and the elementary steps involved. The examples in this review highlight the need for further research on: (i) diesel engine performance and emissions when using OME with or without diesel; (ii) new reactants combinations; (iii) efficient catalysts in more methodical studies; (iv) reaction mechanisms and elementary steps.

A more viable process requires the development of more efficient catalysts, the design of simpler reaction pathways and the search for applications for a wider OME range i.e. outside the three to five chain length range. Alternatively, OME outside this range can be recycled and equilibrated to the desired chain length according to the SF distribution. In an environment with ever tightening emission regulations and the lack of alternatives to liquid fuels for long-distance transport, OME are promising substitutes to the traditional fossil fuels and first generation biofuels. They thus offer a potential solution for a sustainable future mobility.

Acknowledgements

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